Anomalous Acoustoelectric Effect in $La_{0.67}Ca_{0.33}MnO_3$ Films

Y. Ilisavskii,[1] A. Goltsev,[1] K. Dyakonov,[1,*] V. Popov,[1] E. Yakhkind,[1] V. P. Dyakonov,[2,3] P. Gierłowski,[2] A. Klimov,[2] S. J. Lewandowski,[2] and H. Szymczak[2]

[1]*A. F. Ioffe Physical-Technical Institute, Politekhnicheskaja 26, St. Petersburg 194021, Russia*
[2]*Institute of Physics, Al. Lotników 32/46, 02-668 Warszawa, Poland*
[3]*A. A. Galkin Physico-Technical Institute, R. Luxemburg 72, Donetsk 340114, Ukraine*
(Received 17 December 2000; published 17 September 2001)

We have studied the acoustoelectric (AE) effect produced by surface acoustic waves (SAW) in a monolithic layered structure, composed of a piezodielectric $LiNbO_3$ substrate and a $La_{0.67}Ca_{0.33}MnO_3$ film. The experiments unexpectedly revealed in the longitudinal AE effect an anomalous contribution, invariant upon reversal of SAW propagation, which coexists with the ordinary (odd in wave vector) effect. The anomalous effect dominates near the metal-insulator transition, while the ordinary effect prevails at high and low temperatures. We show that the anomalous effect is caused by strong modulation of the film conductivity produced by the SAW elastic deformations.

DOI: 10.1103/PhysRevLett.87.146602 PACS numbers: 72.50.+b, 75.30.Vn, 77.65.Dq

The mixed-valence perovskite manganese oxides $R_{1-x}A_xMnO_3$, where $R =$ La, Nd, Pr, and $A =$ Ca, Sr, Ba, Pb, have been the subject of intense experimental and theoretical studies over the past several years. These compounds attract much attention not only because they exhibit a rich variety of strongly interrelated magnetic, structural, and electronic properties, but also because of possible technical applications. These studies have shown that the properties of manganites are determined not only by the double-exchange mechanism [1] but also by strong electron-phonon interaction [2] of the Jahn-Teller type. The latter mechanism is responsible for polaronic states with thermally activated transport in the paramagnetic state, while the double exchange leads to a ferromagnetic transition at a critical temperature T_c, accompanied by a change from a semiconductorlike behavior above T_c to a metalliclike one below T_c. There are several direct experimental observations, which confirm the above outlined general picture (see, e.g., the review by Coey *et al.* [3] and references therein). The recently observed large pressure effect on the transport and magnetic properties of manganites [4] also is in agreement with the strong electron-phonon coupling. However, there still remain many open and unsolved problems.

In this Letter we report on the investigation of the acoustoelectric (AE) effect in $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) thin films, which was undertaken primarily in order to obtain independent experimental evidence concerning the conduction mechanism and the type of charge carriers in manganites. We have investigated a monolithic layered structure composed of piezodielectric $LiNbO_3$ (LNO) monocrystalline substrate onto which was deposited a suitably patterned LCMO thin film. The film was penetrated by a surface acoustic wave (SAW) launched into the substrate.

The SAW drags free charge carriers due to the momentum transfer from the acoustic wave to the carriers thus producing in the LCMO film either acoustoelectric voltage or current, depending on whether the film is open- or short-circuited. In our structure, charge carriers are affected both by a deformation wave and piezoelectric field, which accompany the propagating SAW. This is in contrast to earlier experiments, in which the investigated sample was subject only to the piezoelectric field [5]. Because of the SAW localization near the substrate-film interface, the deformation amplitude in the film can reach 10^{-3}, equivalent to the pressure of 0.1 GPa. This oscillating pressure causes in turn a modulation of the film conductivity.

We have found that the AE current displays a strong temperature dependence peaking in the vicinity of the metal-insulator (M-I) transition. However, the most intriguing result is the observation of two contributions to the AE current. Besides the ordinary AE current, which is odd in the SAW wave vector, i.e., it changes its sign upon reversal of the SAW direction of propagation, we have observed also an anomalous—even in the wave vector—current component. The sign of the ordinary AE current in the whole temperature range was found to be in agreement with hole-like conductivity. The anomalous AE current, as we show further on, is related to the strong pressure dependence of the manganite film conductivity. This is supported by the fact that in a different experimental arrangement only the ordinary AE effect has been observed [5]. The even longitudinal AE effect has been studied in several situations (e.g., piezoelectrics with traps [6], and asymmetric ballistic channels [7]), but these studies clearly are not pertinent in our case. Our manganite films are spatially homogeneous and contain no traps. Moreover, geometrical factors have been checked and excluded. Some parallels can be drawn only to the first theoretical study of the even acoustoelectric effect, carried out for crystals without the center of inversion [8]. Our films have such center but are in intimate contact with a substrate lacking this property. To the role of symmetry we revert further on.

The LCMO films, 100 to 200 nm thick, were laser ablated from a ceramic $La_{0.67}Ca_{0.33}MnO_3$ target and grown at

730 °C on $+y$-cut LNO substrates without postannealing. After deposition the films were patterned photolithographically and etched into a Hall bar 10 mm long and 2 mm wide. X-ray diffraction investigation shows that the films are single phase, epitaxial, and (211) oriented with the pseudocubic lattice parameter $a_0 = 0.3853$ nm. Chemical composition of the films was found from electron probe microanalysis (EPMA) to be identical to that of the target, within an experimental error of 2%. The spatial and electrical homogeneity of the films was verified by the EPMA scanning and resistive measurements performed at different parts of the samples.

The AE effect studies have been carried out by launching the Rayleigh surface acoustic waves along the surface of the LNO substrate (see Fig. 1). The SAW pulse was generated and detected by two interdigital transducers (IDT), positioned at the edges of the substrate with the LCMO film deposited centrally between them. The pulse duration τ was varied from 1 to 7 μs and the pulse repetition rate was kept constant at 50 Hz. The transducer aperture (3 mm) was larger than the film width and, therefore, the acoustic wave was spreading over the whole film. During the AE studies the possible role of spurious effects, such as rectification of stray radio frequency (rf) fields induced by the IDTs in film contacts, the SAW diffraction and geometrical effects, has been checked and excluded. The AE effect has been studied in the short-circuit geometry at the SAW frequency of 87 MHz ($\lambda = 40$ μm). The AE current between the film contacts has been determined by measuring the voltage drop across a load resistor using a video amplifier and an oscilloscope.

The resistivity $\rho(T)$ of the investigated LCMO films attains a maximum at 220 K (Fig. 2). According to ac susceptibility measurements employing a mutual inductance method, the resistivity peak takes place near the ferromagnetic phase transition (see the inset in Fig. 2). Low values of room temperature and residual resistivities (20 mΩ cm and ~500 $\mu\Omega$ cm at 4.2 K, respectively) and the sharpness of the $\rho(T)$ peak indicate the absence of significant grain boundary contributions to the resistivity. An applied magnetic field H shifts the $\rho(T)$ peak towards higher temperatures and markedly increases the film conductivity, resulting in a colossal magnetoresistance effect: $\mathrm{MR} = [\rho(H) - \rho(0)]/\rho(0) \sim -80\%$ at 25.5 kOe.

Results of the longitudinal acoustoelectric effect measurements in the LCMO films are shown in Fig. 3(a), where full circles mark the temperature dependence of the AE current I_{AE} in a zero magnetic field for a sound wave vector $\mathbf{q}$ parallel to the $+z$ axis of the substrate (this direction is distinguished due to the lack of the center of inversion in LNO). At $T = 300$ K the value of I_{AE} is about 2 μA for the SAW intensity $\Phi \sim 3$ W/cm. I_{AE} increases with decreasing temperature and approaches its maximum value of about 25 μA near the *M-I* transition. With a further decrease in temperature the AE current is reduced to ~1 μA at $T \approx 77$ K.

As already remarked, the ordinary longitudinal acoustoelectric effect should be odd with respect to the SAW wave vector $\mathbf{q}$ [9]. In order to check this assertion, we performed separate measurements with reversed direction of SAW propagation by switching the rf source to the other transducer, so that $\mathbf{q}$ was antiparallel to the $+z$ axis. The acoustoelectric current I_{AE} measured in this manner exhibited an unexpected and puzzling behavior shown in Fig. 3(b) by full circles. As seen, I_{AE} displays a complex temperature dependence and undergoes twice a sign reversal at temperatures near the *M-I* transition.

Such an unexpected dependence of I_{AE} on the $\mathbf{q}$ direction can be explained if two contributions to the AE current are assumed to exist: $I_{\mathrm{AE}} = I_{\mathrm{even}} + I_{\mathrm{odd}}$. The first term is anomalous and even in $\mathbf{q}$, while the second one is ordinary and odd. We have separated both these contributions using experimental data and the relations: $I_{\mathrm{odd}}(-\mathbf{q}) = -I_{\mathrm{odd}}(\mathbf{q})$, $I_{\mathrm{even}}(-\mathbf{q}) = I_{\mathrm{even}}(\mathbf{q})$. The results are displayed in Figs. 3(a) and 3(b). One can see that the anomalous longitudinal AE effect dominates near the *M-I* transition and its magnitude exceeds the ordinary longitudinal AE effect approximately twice. It should be remarked that the anomalous I_{AE} is always directed along

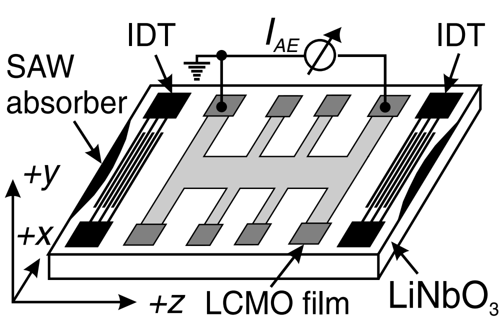

FIG. 1. Schematic drawing of the investigated structure showing the $LiNbO_3$ substrate, $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) film deposited on the substrate, and interdigital transducers (IDT). The coordinate system refers to the $LiNbO_3$ crystallographic axes.

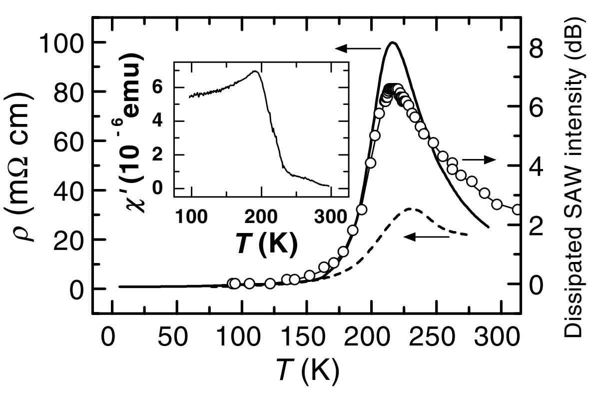

FIG. 2. Sample resistivity versus temperature at $H = 0$ (solid line) and $H = 25.5$ kOe (dashed line), and SAW dissipation in the LCMO-LNO layered structure at $H = 0$ (open circles). Inset: ac susceptibility measured using in-plane ac magnetic field of 5 Oe at 625 kHz versus temperature.

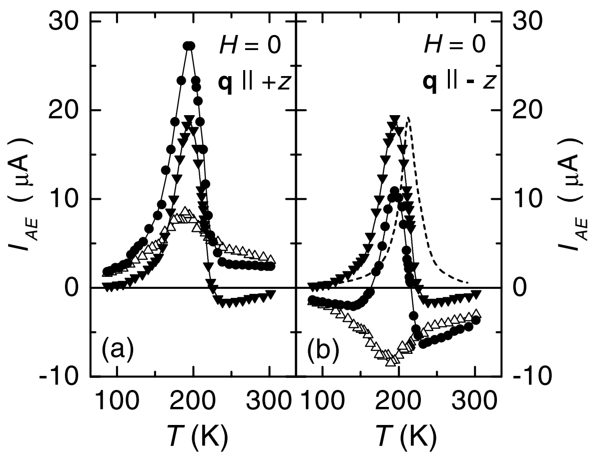

FIG. 3. Acoustoelectric current I_{AE} versus temperature in a $La_{0.67}Ca_{0.33}MnO_3$ film at $H = 0$ for two orientations of the SAW wave vector **q** with respect to the $+z$ axis of $LiNbO_3$: (a) parallel and (b) antiparallel. •: Total AE current; ▼: the anomalous (even) contribution to I_{AE}; △: the ordinary (odd) contribution to I_{AE}; – – –: the even AE current calculated from Eq. (5). The solid lines are a guide for the eye.

the $+z$ axis. The ordinary AE effect prevails at high and low temperatures, and its sign corresponds to the holelike conductivity in the whole investigated temperature range, as is expected in the case of partial substitution of trivalent La by divalent Ca.

To verify the acoustoelectric nature of the observed effects, we have investigated in detail the dependence of I_{AE} on both Φ and τ. These measurements have shown, as expected, that at all temperatures I_{AE} depends linearly on Φ, while the initially linear dependence of I_{AE} on τ saturates for $\tau > 2.5$ μs, when the spatial length of the SAW pulse becomes larger than the film length.

To analyze the interaction of the SAW with the thin manganite film in mechanical contact with the LNO substrate we apply the coordinate system with the positive y axis normal to the film (see Fig. 1). The boundary plane is the xz plane. The manganite film has a thickness a; thus the free surface of the film is the plane $y = a$. The SAW of frequency ω propagates in the piezodielectric substrate along the z axis and is accompanied both by an electric field $\mathbf{E}(y, z, t)$ and strain $S_{ij}(y, z, t)$. In our geometry, only the y and z components of **E** and the lattice displacement are nonzero. **E** generates in turn a local current density $J_i(y, z, t) = \sigma_{ij}(y, z, t)E_j(y, z, t)$ in the film, where σ_{ij} is the tensor of the film conductivity (in the long-wavelength limit the diffusive contribution to the current may be omitted). At the acoustic frequencies used ($\omega \sim 10^8$ s^{-1}), the dependence of σ on ω may be neglected, as the strong frequency dependence of the polaronic conductivity is expected to occur at $\omega \sim (4/\hbar)\mathbb{E}_a \sim 10^{13}$ s^{-1} (see, e.g., [10]), where $\mathbb{E}_a \sim$ 120 meV is the polaronic activation energy in LCMO.

E and S_{ij} induce a local modulation of σ_{ij}:$\sigma_{zz}(y, z, t) = \sigma_0 + \sigma_1(y, z, t) + \sigma_2(y, z, t)$, where σ_0 is the unperturbed conductivity, $\sigma_1(y, z, t) = n_s(y, z, t)\partial\sigma_0/\partial n$, representing the effect of electric field **E**, is due to the modulation of charge carrier concentration $n = n_0 + n_s$, $n_s \ll n_0$ by **E** (the influence of **E** on the drift mobility may be neglected), and the last term

$$\sigma_2(y, z, t) = \sigma_0[\Pi_{3333}S_{zz} + \Pi_{3322}S_{yy} + \Pi_{3323}S_{yz}]$$

describes the modulation of σ_{zz} by the strain. The tensor $\Pi_{ijkl} \equiv \partial \ln\sigma_{ij}/\partial S_{kl}$ calculated at $S_{kl} = 0$ and at fixed temperature describes the effect of strains on σ_{ij}. The changes of drift mobility and electron concentration both contribute to Π_{ijkl}. The pseudocubic symmetry of LCMO allows one to put $\Pi_{3323} = 0$, and for the other two terms we simplify the notation to $\Pi_{3333} \equiv \Pi_{33}$ and $\Pi_{3322} \equiv \Pi_{32}$.

The longitudinal AE current per unit length in the x direction generated by the SAW in the film is by definition

$$\begin{aligned} j_{ae} &= \frac{1}{\Theta}\int_0^{\Theta} dt \int_0^a dy\, J_z(y, z, t) \\ &= \frac{1}{\Theta}\int_0^{\Theta} dt \int_0^a dy\, (\sigma_1 E_z + \sigma_2 E_z) \equiv j_{ae}^{(1)} + j_{ae}^{(2)}, \end{aligned} \tag{1}$$

where $\Theta = 2\pi/\omega$. In order to calculate j_{ae} it is necessary to find the relations between E_z, S_{ij} and n_s, imposed by Maxwell's equations and mechanical-piezoelectric equations of state, and by the boundary conditions at the surfaces $y = 0$ and $y = a$. The thickness a of our film is small compared to the acoustic wavelength λ but is still much larger than the Debye length λ_D, i.e., $\lambda_D \ll a \ll \lambda$. In the broad temperature region around the $\rho(T)$ peak, the conductivity of the manganite film is small, close to that of semiconductors. Therefore, we can apply Ingebrigtsen's approach [11] and assume that the electric field of the SAW produces at the film surfaces $y = 0$ and $y = a$ surface charges due to the screening effect; these charges produce in turn surface currents. The dc component of the total surface current per unit length in the x direction is the current $j_{ae}^{(1)}$:

$$j_{ae}^{(1)} = q\Gamma\Phi\sigma_0(e\omega n_0)^{-1}, \tag{2}$$

where e is the charge of charge carriers, Φ is the SAW intensity, and Γ is the attenuation [$\Phi = \Phi_0 \exp(-\Gamma z)$]:

$$\Gamma = \frac{2\pi}{\lambda} K^2 \frac{\sigma_\square/\sigma_m}{1 + (\sigma_\square/\sigma_m)^2}, \tag{3}$$

where K^2 is the electromechanical coupling coefficient, $\sigma_\square = a\sigma_0$ is the sheet conductivity, and σ_m is a material constant [11]. $j_{ae}^{(1)}$ is odd in q and represents the ordinary longitudinal AE current [9,12]. Equation (3) describes very well the observed SAW attenuation (Fig. 2). A noticeable deviation of the experimental dependence $\Gamma(T)$ from Eq. (3) occurs only at temperatures approximately 30 K below the M-I transition.

In order to calculate the current $j_{ae}^{(2)}$ due to the film deformation, it is necessary to evaluate the quantities S_{ij} and E_z in the film, taking into account their continuity at $y = 0$. Since the film is thin ($aq \ll 1$), we can assume that S_{zz} changes weakly within $0 < y < a$, i.e., $S_{zz}(y,z,t) \approx S_{zz}(0,z,t)$. The strain S_{yy} may be estimated as $S_{yy}(y,z,t) \approx -\nu S_{zz}(0,z,t)$, which is exact at the free surface $y = a$ and $\nu = c_{12}/c_{11} \approx 0.4$ [13], where c_{11} and c_{12} are the components of the elastic tensor of the LCMO film. In LNO the strain S_{zz} is related to the electrical displacement D_z and electric field E_z by $D_z = \varepsilon_{33}E_z + p_{33}S_{zz}$, where ε_{33} and p_{33} are components of the dielectric and piezodielectric tensor, respectively (we assumed $p_{32} = 0$, as this parameter weighs about 1% in our results). In this manner, Eq. (1) gives

$$j_{ae}^{(2)} = \frac{a\sigma_0}{p_{33}}(\Pi_{33} - \nu\Pi_{32})\frac{1}{\Theta}\int_0^{\Theta} dt \times [D_z(+0,z,t) - \varepsilon_{33}E_z(0,z,t)]\overline{E}_z(z,t), \quad (4)$$

where $\overline{E}_z(z,t)$ is the electric field averaged over the film thickness. For $aq \ll 1$ we have $\overline{E}_z(z,t) \approx E_z(0,z,t)$. We estimated the contribution of D_z to $j_{ae}^{(2)}$ in Eq. (4) and found that D_z can be neglected if $1 \ll \sigma_0/\varepsilon\omega \ll 1/(\lambda_D q)$, where ε is the static dielectric constant of the film. Using the relation $E_z(0) = iq\varphi(0)$ and expressing the surface potential $\varphi(0)$ in terms of Φ and Γ, we obtain from Eq. (4)

$$j_{ae}^{(2)} = -\Gamma\Phi\varepsilon_{33}(\Pi_{33} - \nu\Pi_{32})/p_{33}. \quad (5)$$

This result clearly demonstrates that $j_{ae}^{(2)}$ is even in q, and its direction is determined by the signs of p_{33} and Π_{3i}. It is interesting to note that the current $j_{ae}^{(2)}$ is bulk, unlike the surface current $j_{ae}^{(1)}$. The coefficients Π_{3i} are related to the pressure dependence of the conductivity: $2\Pi_{32} + \Pi_{33} = -3\kappa^{-1}\partial\ln\sigma_0/\partial P$, where κ is the film compressibility. According to the pressure experiments, in LCMO [4] the quantity $\partial\ln\sigma_0/\partial P$ is positive, which means negative Π_{3i}, and has a pronounced temperature dependence: it is small at high and low temperatures but peaks to about 3.5 $[\mathrm{GPa}]^{-1}$ at a temperature slightly lower than that of the resistivity peak. For numerical estimation we approximate $\Pi_{33} \approx \Pi_{32}$. Using $\kappa^{-1} = 85$ GPa [14] we find $\max\Pi_{ij} \sim -300$.

It should be observed from Eq. (5) that the appearance of the even AE effect requires a pressure dependent film conductivity ($\Pi_{3i} \neq 0$), piezoelectric properties of the substrate ($p_{33} \neq 0$), and the existence of a distinguished direction in the substrate.

The above outlined theory is in good agreement with the experimental data. As the coordinate z axis is chosen to be parallel to the $+z$ crystallographic axis, the constant p_{33} is positive [15] and, according to Eq. (5), $j_{ae}^{(2)}$ flows along the $+z$ axis. Substituting the well known parameters of LNO and our own experimental result $\max\Gamma \sim 2\ \mathrm{cm}^{-1}$ into Eq. (5), we find $\max j_{ae}^{(2)} \sim 30\ \mu\mathrm{A/cm}$ for $\Phi \sim 3$ W/cm. The experimental data in Fig. 3 correspond to $\max j_{ae}^{(2)} \sim 100\ \mu\mathrm{A/cm}$. Taking into account the approximate character of our estimations of Γ, Φ, and Π_{3i}, we consider the agreement between the theory and experiment as satisfactory. Equation (5) also describes very well the temperature behavior of $j_{ae}^{(2)}$, as shown in Fig. 3(b). The theoretical curve shown there, normalized to the experimental maximum, was calculated from Eq. (5) using experimental dependencies $\Gamma(T)$ (Fig. 2) and $\partial\ln\sigma_0/\partial P$ from pressure measurements [4]. The observed maximum of $j_{ae}^{(2)}$ is shifted towards lower temperatures by approximately 15 K with respect to the theoretical prediction. This shift may be caused by a possible difference in temperature of the peak of $\partial\ln\sigma_0/\partial P$ between our LCMO films and bulk samples [4]. It should be noted that also the order of magnitude of the odd AE current $j_{ae}^{(1)}$ estimated from Eq. (2) agrees with the experiment.

In conclusion, we have observed two contributions to the longitudinal acoustoelectric effect produced by surface acoustic waves in $La_{0.67}Ca_{0.33}MnO_3$ films. The anomalous, or even in the acoustic wave vector, AE effect is dominant near metal-insulator transition, where it exceeds a few times the ordinary (odd) AE effect. The ordinary AE effect prevails at high and low temperatures, and its sign corresponds to holelike conductivity. The anomalous AE effect is shown to be due to a strong modulation of the film conductivity produced by elastic deformations carried by the acoustic wave. Such an effect can be expected also in other conducting materials, which exhibit similar pressure dependence of conductivity.

This work was supported in part by Polish Government (KBN) Grants No. 2 P03B 139 18 and No. PBZ-KBN-013/T08/19 and by the Russian Foundation for Basic Research Grants No. 99-02-18333 and No. 01-02-17479.

*Electronic address: K.Dyakonov@pop.ioffe.rssi.ru

[1] C. Zener, Phys. Rev. **82**, 403 (1951).
[2] A. J. Millis, P. B. Littlewood, and B. I. Shraiman, Phys. Rev. Lett. **74**, 5144 (1995).
[3] J. M. D. Coey, M. Viret, and S. von Molnár, Adv. Phys. **48**, 167 (1999).
[4] J. J. Neumeier *et al.,* Phys. Rev. B **52**, R7006 (1995).
[5] Li Wang *et al.,* Phys. Rev. B **60**, R6976 (1999).
[6] A. I. Morozov, JETP Lett. **2**, 228 (1965).
[7] O. Entin-Wohlman *et al.,* Phys. Rev. B **62**, 7283 (2000).
[8] V. L. Gurevich and A. L. Efros, Sov. Phys. JETP **17**, 1432 (1963); V. L. Gurevich, Sov. Phys. Semicond. **2**, 1299 (1969).
[9] G. Weinreich, Phys. Rev. **107**, 317 (1957).
[10] H. G. Reik, Solid State Commun. **1**, 67 (1963).
[11] K. A. Ingebrigtsen, J. Appl. Phys. **41**, 454 (1970).
[12] The deformation potential interaction of charge carriers with the SAW gives an additional contribution to the odd AE current. In manganites this term can be neglected, because even at very low temperatures λ is much larger than the mean free path of charge carriers.
[13] C. Zhu and R. Zheng, J. Appl. Phys. **87**, 3579 (2000).
[14] C. Zhu *et al.,* Appl. Phys. Lett. **74**, 3504 (1999).
[15] R. T. Smith and F. S. Welsh, J. Appl. Phys. **42**, 2219 (1971); R. A. Graham, J. Appl. Phys. **48**, 2153 (1977).